**TRANSLATION**
of DE-OS 101 29 305 A1

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**Method of producing three-dimensional patterns**

The use of surface-modified powders of thermoplastic materials results, in the case of rapid prototyping by laser sintering, in models having an improved surface finish, a higher level of detail and an increased accuracy of contour.

Description

**[0001]** The invention relates to a method of rapid prototyping by laser sintering using surface-modified powders of thermoplastic materials.

**[0002]** The term rapid prototyping combines the computer-controlled additive, automatic model-building methods known today. Laser sintering denotes a rapid prototyping method in which fills of particular powder materials are heated and sintered in layers at particular positions of planes by the action of laser beams which are preferably controlled by a program.

**[0003]** The use of thermoplastic powders for laser sintering by means of laser is known (A. Gebhardt, Rapid-Prototyping, Carl Hanser Verlag, Muenchen, Wien 2000, page 127). A method of producing model members is described in which, by using fine-sized thermoplastics, with the aid of the light of a laser, for instance a $CO_2$ or ND/YAG laser, any three-dimensional structure can be built up by selective sintering.

**[0004]** It is further known that thermoplastic or plastic powders in which the individual particles are spherical are excellently suited for laser sintering.WO/97/29148 describes the production of spherical particles of styrene and acrylate polymers by spray-drying as well as the use of the products obtained for laser sintering.

**[0005]** From DE 198 20 725 A 1 the use of beaded homo- or copolymers of mono-ethylenically unsaturated compounds is known for laser sintering.

**[0006]** In numerous cases the use of partly crystalline polymers is desirable for the production of models by laser sintering. Models of partly crystalline polymers show, compared to models made of amorphous polymers, a higher degree of non-porosity and a higher mechanical strength.

**[0007]** In the doctor's thesis by Gabriele Alscher, Das Verhalten teilkristalliner Thermoplaste beim Lasersintern[1], Shaker publishing house, Aachen 2000, pages 31-32, the advantages of isothermal laser sintering are discussed in detail.

**[0008]** The density, the surface finish, the level of detail and the accuracy of contour of the model are largely determined by the properties of the polymer powder in rapid prototyping by laser sintering.

**[0009]** In certain cases of application the currently used polymer powders have dissatisfying results, i.e. a poor surface finish, a low level of detail and a low contour accuracy. This drawback requires complicated re-finish of the prototype to obtain the surface finish necessary in practice.

**[0010]** It is another drawback of the previously executed laser methods that the thermoplastic powders used show a tendency to agglomeration during storage and use by virtue of the increased temperature even without exposure to laser. Due to this tendency to agglomeration, the powders employed in a laser sintering process but not used up for the model generation can be used only partly in a subsequent laser sintering process. For this reason, new powders not yet utilized in a laser sintering process are always admixed to the powders that are further used. The amount of new powder added to the recycling material must amount to at least 33 % by weight, according to Bernd Keller, Rapid-Prototyping: Grundlagen zum selektiven Lasersintern von Polymerpulvern[2]; Shaker publishing house: Aachen 1999, pp. 110-112, in order to obtain a sufficient building process safety during laser sintering.

**[0011]** It is the object of the present invention to provide thermoplastic particles for laser sintering which result in molded bodies having improved surface finish, higher level of detail and increased contour accuracy. It is another object to provide thermoplastic particles that have a lower tendency to agglomeration at the non-exposed positions during the laser sintering process.

**[0012]** The subject matter of the present invention is a method of producing three-dimensional patterns by laser sintering using thermoplastic particles having an average particle size of 5 to 250 µm for rapid prototyping by laser sintering, which is characterized in that the surface of the particles is modified prior to laser sintering to reduce the wettability thereof.

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[1] The behavior of partly crystalline thermoplastics during laser sintering

[2] Principles on selective laser sintering of polymer powders

**[0013]** The thermoplastics taken into consideration for the method are the usually thermoplastically processable polymers, exemplified are polystyrene, polycarbonate, thermoplastic polyurethanes, polyamides and polyesters.

**[0014]** Partly crystalline thermoplastics are preferably employed. In the present context, partly crystalline thermoplastics are synthetic polymers having at room temperature an at least partial crystallinity and melting within the range of from 100 to 300°C. Thermoplastics selected from the group of polyamides, polyesters and polyurethanes are preferred. Polyamide-6,6, polyamide-6,10, polyamide-6, polyamide-7, polyamide-8, polyamide-9, polyamide-11, polyamide-12 and appropriate copolymers of these components are used as partly crystalline polyamides. Polyamide-11 and polyamide-12 are especially preferred.

**[0015]** The particle size of the thermoplastic particles amounts to 5 to 250 µm, preferably 10 to 100 µm. To define the particle diameters (particle size) the average weight is indicated in this case. The thermoplastic particles may have a narrow or wide distribution of particle diameters. Thermoplastic particles having a narrow distribution of particle diameters are of advantage to specific applications.

**[0016]** The thermoplastic particles may have an irregular shape, e.g. a splint shape or a spherical shape. The use of particles in spherical shape involves advantages, e.g. with respect to the free-flowing property of the powders and the pore volume of the models.

**[0017]** The method is preferably applied to isothermal laser sintering.

**[0018]** In accordance with the invention, the wettability of these particles is reduced by a surface modification of the thermoplastic particles. In this context, wettability means the tendency of a liquid to cover the surface. For describing the wettability as to quantity, the contact angle can be considered in this case. The contact angle in general may have values ranging from 0° to 180°, the value 0° denoting complete wetting (spreading) and 180° denoting no wetting. The contact angle can be calculated, e.g., from the surface energy according to the Washburn method which is directly measured from powders. Further details of this method were described by Christopher Rulison: Wettability Studies for Porous Solids including Powders and Fibrous Materials; Technical Note #302, Kruess USA, Hamburg.

**[0019]** The surface modification should preferably increase the contact angle by at least 10° vis-à-vis the non-treated thermoplastics.

**[0020]** The size of the contact angle is a function of the wetting liquid. It has turned out in comprehensive test series that the use of N-methyl-2-pyrrolidone as test liquid provides values for the contact angle that permit a relevant statement concerning the use of the powder examined as material for laser sintering. N-methyl-2-pyrrolidone is a telling test liquid also because at room temperature the surface tension of N-methyl-2-pyrrolidone has the same value as molten polyamide 12, a particularly important material for laser sintering, at the melting temperature of PA 12. The contact angle is increased by the surface modification.

**[0021]** All basically known physical and chemical methods of reducing the wettability are taken into consideration for modification. As physical methods especially ultrasonic treatment and treatment by electromagnetic radiation of different wavelengths or by particle radiation (electron radiation) are mentioned in this context. Corona and plasma treatments, too, are further physical methods of surface modification.

**[0022]** Preferred are also chemical methods, especially (reactive, where appropriate) coatings with an ionic or non-ionic surfactant, the coating with a polymer compound and the treatment with a silane.

**[0023]** Also combinations of the physical and chemical treatment methods are preferred.

**[0024]** Suited surfactants are listed in "Surfactants Europe, A Directory of Surface active Agents available in Europe" (Edited by Gordon L. Hollis, Royal Society of Chemistry, Cambridge (1995)). Surfactants having a linear or branched $C_6$ to $C_{24}$ alkyl group are preferred. Moreover, surfactants including siloxane units are utilized. Especially well suited are fluorosurfactants, in particular surfactants having a $C_4$ to $C_{18}$ perfluoroalkyl residue.

**[0025]** The amount of surfactant is especially 0.001 % by weight to 5 % by weight, preferably 0.01 % by weight to 1 % by weight related to the thermoplastic particles.

**[0026]** The surface modification of the thermoplastic particles by surfactant takes place such that the non-treated particles are brought into contact with a solution of the surfactant and the solvent is removed. In many cases water is a suitable solvent. The solvent can be removed by evaporation, where appropriate at an increased temperature of 100°C or by applying reduced pressure, for instance 5 to 200 torr.

**[0027]** Suitable surface-active polymer compounds for treating thermoplastics are polymers soluble in non-aqueous solvents having a molecular weight of 2,000 to

1,000,000. Preferred are polymers having a share of polymerized units of $C_8$ to $C_{22}$ alkyl(meth)acrylates and/or vinyl esters of $C_8$ to $C_{22}$ carbonic acids. By way of example polymers having polymerized units of stearylmethacrylate, laurylmethacrylate and vinylstearate are mentioned. Especially suited are copolymers of $C_8$ to $C_{22}$ alkyl(meth)acrylates or vinyl esters of $C_8$ to $C_{22}$ carbonic acids having hydrophilic monomers. In this context, polymerizable olefinically unsaturated compounds soluble fully or partly (more than 2.5 % by weight at 20°C) in water are understood by hydrophilic monomers. The following examples are mentioned: Acrylic acid and the alkaline and ammonium salts thereof, methacrylic acid and the alkaline and ammonium salts thereof, hydroxyl ethylmethacrylate, hydroxyl ethylacrylate, diethylene glycol monoacrylate, diethylene glycol monomethacrylate, triethylene glycol monoacrylate, triethylene glycol monomethacrylate, tetraethylene glycol monoacrylate, tetraethylene glycol monomethacrylate, glycerol monoacrylate, amino ethylmethacrylate, N,N-dimethyl amino ethylmethacrylate, acryl amide, methacrylic amide, vinyl pyrrolidone and vinyl imidazole. Preferred are amino ethylmethacrylate, N,N-dimethyl amino ethylmethacrylate, acryl amide, methacrylic amide, vinyl pyrrolidone and vinyl imidazole.

**[0028]** Especially preferred polymer compounds are copolymers of

- 75-99 % by weight of $C_8$ to $C_{22}$ alkyl(meth)acrylate and/or vinyl ester of $C_8$ to $C_{22}$ carbonic acids and
- 1-25 % by weight of hydrophilic monomer selected from the group of amino ethylmethacrylate, N,N-dimethyl amino ethylmethacrylate, acryl amide, methacrylic amide, vinyl pyrrolidone and vinyl imidazole.

**[0029]** Further well suited polymer compounds are those having incorporated fluorine groups and perfluoroalkyl groups, e.g. homo- and copolymers of heptafluorobutyl methacrylate.

**[0030]** The quantity of polymer compound amounts to 0.1 % by weight to 20 % by weight, preferably 0.5 % by weight to 7.5 % by weight related to the thermoplastic particles.

**[0031]** The surface modification of the thermoplastic particles by polymer compounds can in turn be carried out in such way that the non-treated particles are exposed to a solution of the polymer compound. A non-aqueous solvent such as, for instance,

isooctane or toluene is suited. The solvent in turn can be removed by evaporation, at an increased temperature, if necessary, or by applying a reduced pressure.

**[0032]** For treatment with silanes, for instance, trimethyl chlorosilane, dimethyl dichlorosilane, hexamethyl disiloxane, propyl trimethoxysilane, gamma aminopropyl trimethoxysilane and mixtures of said silanes are suited.

**[0033]** The treatment with silane can take place without solvent or, what is especially advantageous, in an aprotic solvent. Suitable solvents are, for instance, acetone, butanone, dichloromethane, trichloromethane, toluene, acetic ester or tetrahydrofurane. As a matter of course, a catalyst can be used for silanizing. Protonic acids such as acetic acid or hydrogen chloride as well as amines such as dicyclohexylamine are catalytically active. The coating can also be carried out in the manner that the silane is first hydrolyzed by acid catalysis with e.g. molar amounts of water, wherein the hydrolysable residues X are converted into OH groups and then the freshly prepared OH compound is made to react with the thermoplastic particles in a solvent.

**[0034]** The amount of silane used can be largely varied, it is usually within the range of 0.05 to 10 % by weight, preferably 0.2 to 5 % by weight related to the thermoplastic particles.

**[0035]** The surface-modified powders of thermoplastics according to the invention result in models exhibiting an improved surface finish, higher level of detail and increased contour accuracy in rapid prototyping by laser sintering. The models obtained require no finishing or only to a smaller extent than the models of the present state of the art. Thermoplastic particles which have not been used up during an operating cycle are retained unchanged; especially no agglomerates are formed and they can be completely re-used.

## Examples

### Example 1

### Coating of polyamide powders by polymer compounds

**[0036]** 50 g of polyamide-12 powder having an average particle size of 45 µm are dispersed at a time for 30 minutes at room temperature in 200 ml of a solution of the

below-stated polymer compound in isododecane. After that the isododecane is completely removed at the rotary evaporator at 50°C and under reduced pressure.

| | Polymer compound | Quantity used |
|---|---|---|
| A | Poly(tridecylmethacrylate-co-N-vinylpyrrolidone)-90/10 | 2.5 g |
| B | Poly(tridecylmethacrylate-co-hydroxymethylmethacrylate)-90/10 | 0.5 g |
| C | Poly(tridecylmethacrylate-co-N-dimethylaminoethyl methacrylate)-90/10 | 2.5 g |
| D | Organo-modified siloxane (Tegopren 6846, Goldschmidt) | 0.5 g |
| E | Poly(eicosen-co-N-vinylpyrrolidone)-95/5 | 2.5 g |
| F | Poly(eicosen-co-N-vinylpyrrolidone)-90/10 | 2.5 g |

Example 2

Check-out of modified and non-modified thermoplastic particles

Measurement of contact angle

| Samples | Contact angle with N-methyl-2-pyrrolidone |
|---|---|
| Comparative powder polyamide 12 | 0° |
| Powder from example 1A | 61° |
| Powder from example 1B | 71° |

| Samples | Contact angle with N-methyl-2-pyrrolidone |
|---|---|
| Powder from example 1C | 71° |
| Powder from example 1D | 49° |
| Powder from example 1E | 38° |
| Powder from example 1F | 49° |

**[0037]** The contact angles of the samples modified according to the invention are significantly higher than in the case of non-modified polyamide 12 and prove the reduced wettability.

**[0038]** During sintering the surface-modified powder by means of a $CO_2$ laser an improved surface finish of the sintered material vis-à-vis the samples of non-treated polyamide was obvious.

## Claims

1. A method of producing three-dimensional pattern by laser sintering using thermoplastic particles having an average particle size of 5 to 250 μm, **characterized in that** the surface of the particles is modified prior to laser sintering for reducing the wettability thereof especially by means of physical surface treatment and/or possibly reactive coating with a surface-active substance.
2. Use according to claim 1, characterized in that the contact angle of the surface-modified thermoplastic particles, defined with N-methyl-2-pyrrolidone as test liquid, is increased by at least 10°.
3. A method according to claim 1, characterized in that the thermoplastic particles are coated with an ionic or a non-ionic surfactant.
4. A method according to claim 1, characterized in that the surface-active compound is a polymer compound.
5. A method according to claim 3, characterized in that the surface-active compound is a silane.
6. Three-dimensional models obtained by a method of laser sintering in accordance with any one of the claims 1 to 4.